Evaluation of anaerobic treatment of crude glycerol from biodiesel production in a UASB bioreactor

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Abstract

This study evaluated the use of UASB reactors to treat crude glycerol from a biodiesel industry in comparison with pure glycerol. Two UASB reactors were operated with an OLR of 1 $KgCOD.m^{-3}.d^{-1}$, hydraulic retention time (HRT) of 24 hours, at ambient temperature (15 to 25 ^{o}C), and parameters such as pH, flow rate, temperature, COD (Chemical Oxygen Demand), VSS (Volatile Suspended Solids), VFA (Volatile Fatty Acids), glycerol, 1,3 propanediol and methane production were monitored during 170 days. In addition, batch tests were performed to determine the specific methanogenic activity (SMA) of the sludge, as well as the methanogenic potential of both substrates (MP). During the first 106 days of operation, the UASB reactors were unstable with lower COD removal efficiencies and VFA accumulation. After this period, the reactors have become more stable with COD removal efficiencies as high as 90% and progressively higher SMA values. Crude and pure glycerol showed similar results in terms of COD removal efficiency suggesting that there is no toxicity of the biodiesel effluent used. In addition, the results showed glycerol and 1,3 propanediol did not accumulate in the reactor fed with crude glycerol and that VFA accumulation was lower than 50 $mg.L^{-1}$. In spite of this methane production was much lower than that expected based on SMA estimation, hence nearly 50% of the degraded COD could not be accounted for, indicating there were huge losses of methane in both reactors.

Keywords

Anaerobic digestion; methane production; crude glycerol; biodiesel effluent; anaerobic treatment.

INTRODUCTION

The intensive search for alternative energy sources and sustainable processes in order to reduce environmental pollution and global warming has spurred the global market for clean fuels. The Brazilian government has encouraged the production of Biodiesel, through laws such as the 11097/2005 which establishes the compulsory addition of biodiesel to fuel oil, with a mandatory percentage of 5% of diesel volume from 2013 onwards. Biodiesel production leads to the generation of glycerol as byproduct and several efforts have being made to utilize excess glycerol and produce added value products. In general, 10 kg of glycerol is generated as a by-product for each 100 kg of biodiesel produced (Chi et al 2007). Recently, some studies have been conducted to investigate the anaerobic degradability of crude glycerol focusing on the production of energetic compounds such as methane, hydrogen and methanol (Ito et al 2005, Fountoulakis 2010) or organic compounds such as 1,3-propanediol (Pajuelo-Gonzalez et al 2006, Xiu et al 2007). In this context, the present study investigates the anaerobic degradation of crude glycerol from the biodiesel industry in a lab-scale Upflow Anaerobic Sludge Bed Reactors (UASB).

MATERIAL AND METHODS

Characterization of the biodiesel effluent, crude glycerol, was performed by the following parameters: COD (Chemical Oxygen Demand), BOD (Biochemical Oxygen Demand), oil and grease, volatile suspended solids (VSS), glycerol, chloride, phosphorus, carbohydrates, proteins and lipids; according to standard methodologies (APHA, AWWA, WER, 2005). For the anaerobic treatment, two identical bench scale UASB reactors were used. Reactor R1 was fed with crude glycerol, whereas R2 were fed pure glycerol in a synthetic medium as described elsewhere (Aquino et al 2007). The reactors were kept at room temperature, which varied from 15 to 25^{o}C. The useful bioreactor volume was 3.4 L; the hydraulic retention time (HRT) was 24h and the organic loading rate (OLR) was set at 1.0 $g.L^{-1}.d^{-1}$. The pH inside the reactor was kept around 7.0 with the addition of sodium bicarbonate in the influent (3.75 $g.L^{-1}$). Mesophilic methanogenic sludge from UASB

reactors treating domestic sewage (CePTS, UFMG, Copasa) was used as inoculum. The bench scale reactors performance involved weekly analyses of COD, VFA, VSS, 1,3-propanediol and glycerol. Biogas collection was carried out by using gas bags of 6 L (SUTEL^{TN}, Supelco Analytica) and the analysis of its composition was carried out by gas chromatography (GC-FID, model CP-3380, column DB - WAX (J8W): 30m x 0.25 x mm, Varian). In addition, specific methanogenic activity (SMA) of the sludge and methanogenic potential (MP) of the crude glycerol were performed and compared with those for pure glycerol and glucose. Such tests were performed in glass flasks coupled to manometric measurement of biogas (Ankom^{RF} Gas Production System) using the synthetic medium and inoculum mentioned before. The flasks were incubated at 30°C under continuous stirring (120 rpm) and the absorption of carbon dioxide was carried out by NaOH pellets placed at the top of the flasks, just below the pressure measurement device. The system used is fully automated so that the changes in pressure could be instantly recorded in spreadsheets and then used to assess real time gas production.

RESULTS AND DISCUSSION

Crude glycerol characterization resulted in the following average values: 23.2 g.L^{-1} of protein, 11.4 g.L^{-1} of carbohydrate, 612.1 g.L^{-1} of lipids, 2.0 g.L^{-1} of phosphorus, 5.0 g.L^{-1} of chloride, 582 g.kg^{-1} of glycerol, 828.1 g.L^{-1} of total solids, 89.9 g.L^{-1} of oils and greases, 1,122 g.L^{-1} of COD and 975 g.L^{-1} of BOD. Based on these results, it can be said that crude glycerol is highly concentrated but easily biodegradable (BOD/COD is 0.86), and has a high content of lipids, oil and grease, chlorides and total solids. Assuming that the proteins have 15% of nitrogen, the biodiesel effluent would have a COD:N:P ratio lies in the range of 350:1.1:0.6 to 500:1.5:0.9. Since the ideal COD:N:P ratio for anaerobic microorganisms is from 350:5:1 to 500:5:1, there is a nitrogen and phosphorus deficiency in the crude glycerol, which justifies, in this study, crude glycerol dilution in distilled water (DF = 1,000) and the addition of nutrient solution.

Figure 1 shows the changes in COD during the bioreactors operation. As it can be seen, during the first 106 days the COD effluent from both reactors was quite variable yielding in median COD removal efficiencies of 52% for R1 and 58% for R2. Such a variation was probably due to biomass adaptation for glycerol degradation under the operational conditions. After 106 days, both reactors were apparently more stable since COD removal varied within a narrower range, from 80% to 93% for R1 and from 78% to 96% for R2 (Figure 2).

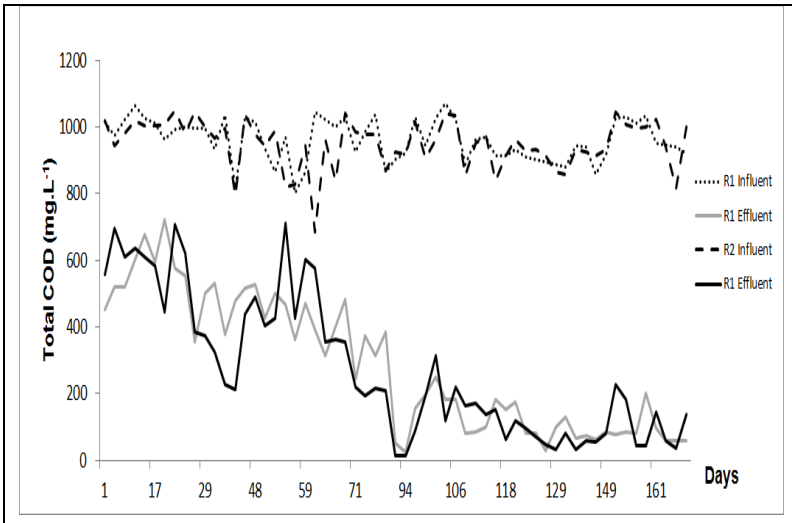

Figure 1. Temporal variation of the concentration of COD influent and effluent of UASB R1 (crude glycerol) and R2 (pure glycerol).

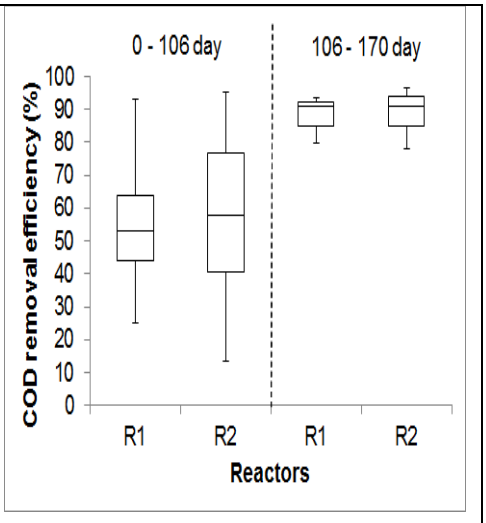

Figure 2: Changes in COD removal efficiency for R1 and R2

Besides being more stable, the residual COD in both reactors was very low, indicating a optimal performance in terms of COD removal. Volatile suspend solids (VSS) data indicates that the sludge accumulation averaged 14.5 g and 13.8 g in reactors R1 and R2, respectively, at the end of the 170

day. Since both reactors were inoculated with 23 g of sludge, it is clearly seen that biomass growth was not impaired in reactor R1, strengthening the hypothesis the compounds present in the biodiesel effluent used was not toxic to anaerobic microorganisms.

Regarding VFA analysis, there was a greater accumulation of these metabolites in both reactors during the first 106 days. In contrast, the concentration of VFA after the biomass adaptation were much lower in both R1 and R2 (Figure 3). Acetic acid was the most predominant VFA throughout reactors operation, and its median concentration decreased from 109 to 19 $mg.L^{-1}$ in R1 and from 125 to 35 $mg.L^{-1}$ in R2, when adaptation and stable periods are compared. As observed for COD, the VFA concentration suggests that R2 was much more instable than R1, leading to higher accumulation of acetic and propionic acids, despite the fact such reactor had been fed with pure glycerol. The significant decrease in the concentration of propionic acid in both reactors may also have contributed to the improvement of COD removal efficiency, since it is considered the most recalcitrant and toxic VFA in the methanogenic environment (Wijekoon et al 2011, Weiland 2010, Marchaim et al 1993).

In terms of biogas production, a total of 46.5 L and 53.8 L were produced (at 0.88 atm, 24°C) for R1 and R2, respectively, during the operational period. The methane percentage in such biogas averaged only 48.7% and 53.8%, respectively. The low methane fraction in the biogas suggest that CO_2 and H_2, which are usual fermentation products, may constitute an important fraction of the biogas composition specially during the biomass adaptation.

In order to perform a mass balance of glycerol degradation, sampling of both reactors were intensified in the last 7 days of operation and the data gathered generated Figures 3 and 4. Figure 3 presents the composition of volatile fatty acids and shows that R1 and R2 exhibited similar pattern of acetic and propionic acids; however R2 led to a higher accumulation of 1,3 propanediol (~5% of the residual COD) and other organic compounds (ex. soluble microbial products – SMP) which would represent almost half of the residual COD (unaccounted for fraction). As it can be seen in Figure 4, there was a high proportion of unaccounted for fraction of degraded COD in both reactors. Considering R1 it is seen that half of the degraded COD was equally distributed to methane and biomass (27.5% and 26.8% respectively) whereas in R2 methane production was a little bit higher than biomass production (32.8% and 22.4%, respectively). Despite this, methane production can be considered low which is probably due to biogas leaks during gas bag manipulation.

To investigate the activity of the methanogenic biomass as well as the potential of the glycerol being converted to methane SMA and MP tests were performed. The tests were carried out with crude (R1) and pure (R2) glycerol and the results (Table 1) were compared with an easily biodegradable substrate (glucose). MP were similar among the three substrates (up to 0.38 $Nm^3.kg^{-1}$) suggesting that conversion of glycerol to methane is similar to glucose. The MP values measured here is in the same range to those reported by Viana et al (2011) for crude glycerol generated from transesterification of different oils.

The SMA results showed that the inoculum sludge fed with pure and crude glycerol performed very similarly and led to methane production which represented 67 and 72% respectively of the SMA obtained when the inoculums sludge was fed with glucose. This is in agreement with Viana et al (2011), who also found that SMA for glycerol was lower than glucose, probably because of the slow rate of glycerol hydrolysis. On its turn, biomass collected from R1 in the last 7 days of operation exhibited SMA values two times as higher when compared to the inoculum and up to three times higher when compared to R2, indicating a strong methanogenic biomass adaption in the reactor fed with crude glycerol. Considering the SMA values of adapted biomass, the methane production in the last 7 days of operation would be 104.5 $gCOD_{CH4}$ in R1 and 32.8 $gCOD_{CH4}$ in R2. However, the actual volume of methane captured and quantified during such period was only 6% in R1 and 21% in R2, indicating there were huge losses of biogas, hence impair the mass balance.

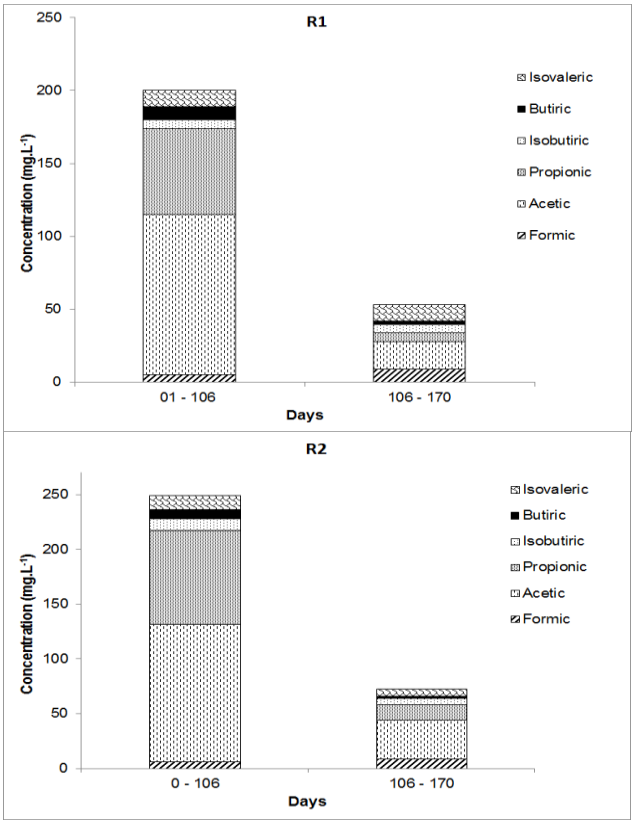

Figure 3. Changes in VFA concentration in effluent of R1 and R2 before and after 106 day.

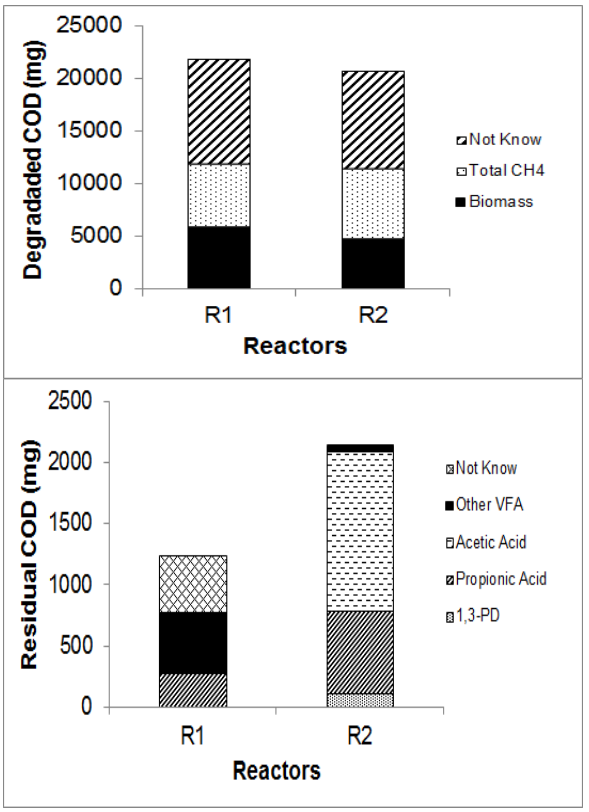

Figure 4. COD mass balance of the last experimental week.

Table 1: SMA, MP and total volume of methane produced in the anaerobic incubation of glucose, glycerol and biodiesel effluent.

	Inoculum sludge		Bioreactor sludge*
Carbon Source	**SMA (gCOD/gVSS.d)**	**MP $Nm^3/(kg_{incubated})$**	**SMA (gCOD/gVSS.d)**
Glucose	0.68 ± 0.07	0.34	-
Pure glycerol (R2)	0.46 ± 0.11	0.38	0.34 ± 0.04
Crude glycerol (R1)	0.51 ± 0.06	0.36	1.03 ± 0.13

*Biomass was collected between 160 and 170 days.

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